"Vapochromic" Compounds as Environmental Sensors. 2. Synthesis and Near-Infrared and Infrared Spectroscopy Studies of $[Pt(arylisocyanide)_4][Pt(CN)_4]$ upon Exposure to Volatile Organic Compound Vapors

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The synthesis, characterization, and vis−NIR−IR vapochromic/spectroscopic studies are reported for isocyanide compounds of the form $[Pt(arylisocyanide)_4][Pt(CN)_4]$ (where arylisocyanide = p-$CNC_6H_4C_nH_{2n+1}$; $n = 1, 6, 10, 12, 14$). The dark blue, solid materials change color in the NIR (near-infrared) spectral region upon exposure to the ambient room-temperature vapor pressure of volatile organic compounds (VOCs). At room temperature the PtPt compounds exhibit strong solid-state absorption and emission bands in the NIR region of the spectrum that are red-shifted from similar bands in the PtPd analogues; ($n = 1$, $\lambda_{\max\ abs} = 744$, $\lambda_{\max\ emit} = 958$; $n = 6$, $\lambda_{\max\ abs} = 841$, $\lambda_{\max\ emit} = 910$; $n = 10$, $\lambda_{\max\ abs} = 746$, $\lambda_{\max\ emit} = 944$; $n = 12$, $\lambda_{\max\ abs} = 764$, $\lambda_{\max\ emit} = 912$; $n = 14$, $\lambda_{\max\ abs} = 690$, $\lambda_{\max\ emit} = 876$ nm). The positions of these broad bands depend on the number of carbons in the alkyl substituent. The absorption and emission bands for the solid material ($n = 10$ compound) also exhibit a substantial red-shift upon cooling to 77 K ($\lambda_{\max\ abs}$ (293 K) = 746; $\lambda_{\max\ emit}$ (293 K) = 944; $\lambda_{\max\ abs}$ (77 K) = 846; $\lambda_{\max\ emit}$ (77 K) = 1094 nm) that is consistent with an alternating cation−anion stacked structure. Qualitatively, compounds with $n > 6$ respond well to nonpolar VOCs; the $n = 1, 6$ compounds respond better to polar VOCs. The shifts observed for $\lambda_{\max\ abs}$ (at 293 K) are on the order of 700 cm^{-1} and are 2−3 times greater than those exhibited by the PtPd analogue compounds under identical conditions. The $n = 10$ compound is the most responsive; the positions of the vis−NIR band in the presence of several solvent vapors are as follows: none, 746 nm; methanol, 757; ethanol, 782; 2-propanol, 782; diethyl ether, 787; acetonitrile, 809; hexanes, 775; acetone, 800; benzene, 801; dichloromethane, 811; chloroform, 837. No response was observed for water vapor. IR studies of films of the $n = 10$ compound on an ATR crystal show that the sorption of VOC by the solid causes no change in the ν(CN) isocyanide stretching frequency but in some cases a substantial shift (0−15 cm^{-1}) in ν(CN) of the cyanide stretch is observed. When the $n = 10$ compound contacts VOCs capable of H-bonding with the $Pt(CN)_4^{2-}$ anion, two cyanide stretches are observed. All the spectroscopic data suggest that the VOC penetrates the solid and interacts with the linear chain chromophore to cause the spectral shifts in the vis−NIR−IR spectral regions. The vapochromic shifts are suggested to be due to dipole−dipole and/or H-bonding interactions between the $Pt(CN)_4^{2-}$ anion and polar VOCs. For nonpolar VOCs, lypophilic interactions between the VOC and the isocyanide ligands that cause no change in the ν(CN) stretching region must cause the NIR vapochromism observed. The absence of a vapochromic response for water vapor is suggested to arise from hydrophobic blocking of the water at the solid/gas interface.

Introduction

The development of rugged, chemical sensor materials has received increasing attention[1] with the growing need to detect volatile organic compounds (VOCs) in the environment and the workplace.[2] Of particular interest are materials that show dramatic and reversible color changes in the visible or near-infrared (NIR) spectral regions upon exposure to VOCs. Ideally, such materials would not only detect VOCs below the part per million (ppm) level but would also show a unique response for each VOC. Responsive compounds that report in the NIR region may be particularly promising because of intrinsic low level background interferences.[3]

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(1) A literature search produced several thousand references in the general area of sensors published between 1993 and 1996. See for example the description of the "Electronic Nose": (a) Persaud, K.; Dodd, G. H. *Nature (London)* **1982**, *299*, 352. (b) Shurmer, H. V. *Anal. Proc. Inc. Anal. Comm.* **1994**, *31*, 39.

(2) The U.S. EPA Environmental Technology Initiative for FY 1994 includes monitoring VOCs as a critical need.

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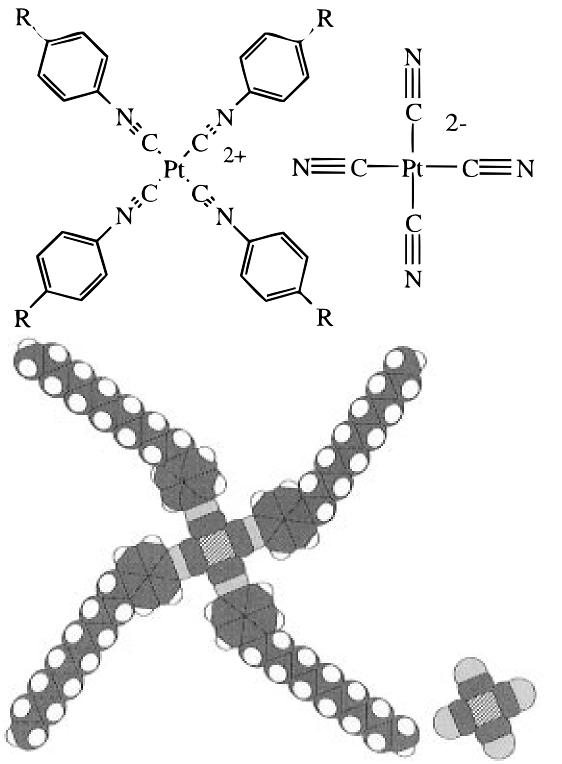

Figure 1. Line drawing and to-scale space-filling models of $[Pt(CNC_6H_4C_{12}H_{25})_4][Pt(CN)_4]$.

Square-planar d^8 complexes that stack in the solid state[4] show promise as sensor materials because they are robust and spectroscopically sensitive to VOC presence.[5] It is well established that the electronic structure of square-planar Pt(II) compounds is often perturbed in the solid state.[6] Crystallization in linear-chain stacks give rise to Pt−Pt interactions that significantly lower the metal-to-ligand charge transfer (MLCT) or $d\sigma^* \rightarrow p\sigma$ energy.[7] Additional absorption shifts have been reported when insoluble double-complex salts ($[PtL_4][PtX_4]$) or Pt(II) are suspended in water or organic solvents.[8] These shifts indicate that the solid-state d^8 stacked structure can be perturbed by interactions with interstitial solvent molecules.

We recently communicated[5] that significant λ_{max} shifts in absorption and emission for $[Pt(arylisocyanide)_4][Pd(CN)_4]$ (where arylisocyanide = p-$CNC_6H_4C_nH_{2n+1}$; $n = 6, 10, 12, 14$) occur upon exposure to VOC vapors. The size mismatch (Figure 1) between the cation and anion complexes apparently produces an open structure that can reversibly sorb VOCs. Incorporation of the VOC into the lattice perturbs the cation−anion stacking structure and causes a shift in the absorption maximum but does not significantly disrupt the crystallinity of the compounds. A striking color change (from pink to blue) was observed for the $n = 10$ PtPd double-complex salt upon exposure to VOCs. In this work, we report the synthesis characterization, and spectroscopic studies of the homometallic analogue complexes $[Pt(arylisocyanide)_4][Pt(CN)_4]$ (where arylisocyanide = p-$CNC_6H_4C_nH_{2n+1}$; $n = 1, 6, 10, 12, 14$). Substitution of $Pt(CN)_4{}^{2-}$ for the $Pd(CN)_4{}^{2-}$ anion enhances the stability of the compounds, lowers the absorption and emission band energies into the NIR spectral region, and gives compounds that show greater "vapochromic" shifts than their $[Pd(CN)_4]^{2-}$ analogues.

Experimental Section

Ligand Synthesis and Characterization. p-$CH_3C_6H_4NC$ was prepared as reported by Ugi and Meyer.[9a] All other aryl isocyanides were prepared from the corresponding amines via the formamide compounds by either a modification of this procedure or that reported by Bringmann ande Schneider.[9b]

p-$C_nH_{2n+1}C_6H_4NHCHO$ (n = 6, 10, 12, 14). The synthesis of p-$C_{10}H_{21}C_6H_4NHCHO$ is given as an example. All other formamides were prepared in an analogous manner. The ^{1}H NMR spectra of formamides have been discussed previously.[10] A mixture of p-$C_{10}H_{21}C_6H_4NH_2$ (5.72 g, 24.5 mmol), 90% formic acid (15 mL), and toluene (100 mL) was stirred and refluxed under a condensor attached to a Dean−Stark water separator for 16 h. As the reaction progressed, the solution color turned from a dark red-brown to pale yellow. Cooling the mixture to 0 °C afforded white flakes of p-$C_{10}H_{21}C_6H_4NHCHO$ (4.91 g, 77%), which were separated from the mixture by filtration. To obtain a second crop of formamide, the solvent was removed from the filtrate under vacuum. The residue was dissolved in a minimum of pentane and cooled to 0 °C to give an additional 1.02 g of p-$C_{10}H_{21}C_6H_4NHCHO$.

p-$C_6H_{13}C_6H_4NHCHO$. Yield = 67%; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C) 8.62 (d, $^3J_{HH}$ = 11.6 Hz, E isomer (H)CONHR), 8.35 (d, $^3J_{HH}$ = 1.6 Hz, Z isomer (H)CONHR; the signal for the E isomer is obscured by the phenyl resonances), 7.88 (br d, Z isomer HCON(H)R), 7.43 (m, Ph), 7.15 (m, Ph), 6.98 (m, Ph), 2.57 (m, $(CH_2)Ph$), 1.58 (m, $(CH_2)CH_2Ph$), 1.29 (m, $((CH_2)_3)CH_2CH_2Ph$), 0.87 (t, $(CH_3)(CH_2)_5Ph$) ppm; IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1693 s.

p-$C_{10}H_{21}C_6H_4NHCHO$. Yield = 95%; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C) 8.64 (d, $^3J_{HH}$ = 11.4 Hz, E isomer (H)CONHR), 8.37 (d, $^3J_{HH}$ = 2.1 Hz, Z isomer (H)CONHR), 7.86 (br d, Z isomer HCON(H)R), 7.45 (m, Ph), 7.21 (br s, E isomer HCON(H)R), 7.16 (m, Ph), 7.01 (m, Ph), 2.59 (m, $(CH_2)Ph$), 1.59 (m, $(CH_2)CH_2Ph$), 1.27 (m, $((CH_2)_7)CH_2CH_2Ph$), 0.89 (t, $(CH_3)(CH_2)_9Ph$) ppm; IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1696 s.

p-$C_{12}H_{25}C_6H_4NHCHO$. Yield = 69%; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C) 8.67 (d, $^3J_{HH}$ = 11.7 Hz, E isomer (H)CONHR), 8.38 (d, $^3J_{HH}$ = 1.8 Hz, Z isomer (H)CONHR), 8.13 (br d, Z isomer HCON(H)R), 7.47 (m, Ph), 7.32 (br s, E isomer HCON(H)R, 7.19 (m, Ph), 7.03 (m, Ph), 2.61 (m, $(CH_2)Ph$), 1.60 (m, $(CH_2)CH_2Ph$), 1.32 (m, $((CH_2)_9)CH_2CH_2Ph$), 0.91 (t, $(CH_3)(CH_2)_{11}Ph$) ppm; IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1698 s.

p-$C_{14}H_{29}C_6H_4NHCHO$. Yield = 85%; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C) 8.62 (d, $^3J_{HH}$ = 11.4 Hz, E isomer (H)CONHR), 8.34 (d, $^3J_{HH}$ = 1.5 Hz, Z isomer (H)CONHR), 8.08 (br d, Z isomer HCON(H)R), 7.42 (m, Ph), 7.29 (br s, E isomer HCON(H)R), 7.13 (m, Ph), 6.98 (m, Ph), 2.56 (m, $(CH_2)Ph$), 1.56 (m, $(CH_2)CH_2Ph$), 1.23 (m, $((CH_2)_{11})CH_2CH_2Ph$), 0.86 (t, $(CH_3)(CH_2)_{13}Ph$) ppm; IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1692 s.

p-$C_nH_{2n+1}C_6H_4NC$ (n = 6, 10). These compounds were prepared by a modification of the method reported by Ugi and

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[4] The prototype is $[Pt(NH_3)_4][PtCl_4]$, Magnus' green salt: (a) Magnus, G. *Pogg. Ann.* **1828**, *11*, 242. (b) Atoji, M.; Richardson, J. W.; Rundle, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 3017. Also see: (c) Connely, N. G.; Crossley, J. G.; Orpen, A. G.; Salter, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1564.

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[7] Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1991**, *30*, 4446.

[8] For ionic stacks see: Little W. A.; Lorentz, R. *Inorg. Chim. Acta* **1976**, *18*, 273. For example, $[Pt(bipy)_2][Pt(CN)_4]$ (bipy = 2,2′-bipyridine) has an absorption λ_{max} of 485 nm in aqueous suspension compared to 514 nm (dry); in an EtOH/benzene suspension, the absorption maximum for $[Pt(phen)_2][Pt(C_2O_4)_2]$ (phen = 1,10-phenanthroline) shifts from 537 (dry) to 575 nm.

[9] Synthesis of isocyanides: (a) Ugi, I.; Meyer, R.; McKusick, B. C.; Webster, O. W. *Org. Synth.* **1961**, *41*, 101. (b) Bringmann, G.; Schneider, S. *Angew. Chem., Int. Ed. Engl.* **1983**, *23*, 139.

[10] (a) Sorensen, O. W.; Scheibye, S.; Lawesson, S.-O.; Jakobsen, H. J. *Org. Magn. Reson.* **1981**, *16*, 322. (b) Rogers, M. T.; LaPlanche, L. A. *J. Phys. Chem.* **1965**, *69*, 3648. (c) Fritz, H.; Kristinsson, H.; Mollenkopf, M.; Winkler, T. *Magn. Reson. Chem.* **1990**, *28*, 331.

Meyer.[9a] The synthesis of p-$C_{10}H_{21}C_6H_4NC$ is given as an example. The hexyl-substituted isocyanide ($n = 6$) was prepared in an analogous manner. Triethylamine was dried over 3 Å molecular sieves and passed through a column of activated neutral alumina before use. A mixture of p-$C_{10}H_{21}C_6H_4NHCHO$ (7.05 g, 27.0 mmol), triethylamine (35 mL, 250 mmol), and CH_2Cl_2 (100 mL) was cooled to 0 °C in an ice-water bath. With stirring, $POCl_3$ (5.0 mL, 54 mmol) was added to the mixture dropwise over 10-min. The mixture was stirred at 0 °C for 1 h, during which the solution color gradually turned from pale yellow to orange-brown. The ice-water bath was removed, and a 25% (w/w) aqueous sodium acetate solution (100 mL) was added to the reaction mixture and stirred for 30 min. The organic (lower) layer was removed, washed three times with a saturated NaCl solution (75 mL each), and dried with anhydrous $CaCl_2$. The solvent was removed by rotary evaporation, and the remaining solid was purified by column chromatography (silica gel column), using a 1:9 mixture of ethyl acetate/CH_2Cl_2 as the mobile phase. Recrystallization from ethanol afforded white needlelike crystals of p-$C_{10}H_{21}C_6H_4NC$ (4.03 g, 61%). ^1H NMR (CD_2Cl_2) 7.28 (d, 2 H, Ph), 7.20 (d, 2 H, Ph), 2.62 (t, 2 H, (CH_2)Ph), 1.58 (m, 2 H, (CH_2)CH_2Ph), 1.26 (m, 14 H, CH_2), 0.88 (t, 3 H, CH_3); IR (CH_2Cl_2) ν(NC) (cm^{-1}) 2128 vs.

p-$C_6H_{13}C_6H_4NC$. After column chromatography, this compound was isolated as a pale-green liquid (71% yield). ^1H NMR (CD_2Cl_2) 7.29 (d, 2 H, Ph), 7.20 (d, 2 H, Ph), 2.62 (t, 2 H, (CH_2)Ph), 1.59 (m, 2 H, (CH_2)CH_2Ph), 1.31 (m, 6 H, CH_2), 0.88 (t, 3 H, CH_3); IR (CH_2Cl_2) ν(CN) (cm^{-1}) 2130 vs.

p-$C_nH_{2n+1}C_6H_4NC$ (n = 12, 14). These compounds were prepared by a modification of the procedure reported by Bringmann and Schneider.[9b] The synthesis of p-$C_{12}H_{25}C_6H_4NC$ is given as an example. The other isocyanide was prepared in an analogous manner. Triethylamine was dried over 3 Å molecular sieves and passed through a column of activated neutral alumina before use. A mixture of p-$C_{12}H_{25}C_6H_4NHCHO$ (10.0 g, 34.5 mmol), triphenylphosphine (9.05 g, 34.5 mmol), and CH_2Cl_2 (250 mL) was cooled to 0 °C in an ice-water bath. To this mixture, an ice-cold solution of $C_2Br_2Cl_4$ (22.5 g, 69.0 mmol) in triethylamine (19.2 mL, 13.8 mmol) was added with stirring. The reaction mixture was stirred for 15 min at −10 °C, then the ice bath was removed, and the mixture was stirred at room temperature for 1 h. After cooling to 0 °C, the mixture was filtered, and the filtrate was washed with H_2O (3 × 50 mL) and saturated aqueous NaCl (2 × 50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation, leaving an oily residue. This was dissolved in warm ethanol (200 mL), and activated carbon was added with stirring. The solution was passed through a Celite column to remove the carbon and cooled to −10 °C to afford white crystals of p-$C_{12}H_{25}C_6H_4NC$ (68%). ^1H NMR (CD_2Cl_2) 7.29 (d, 2 H, Ph), 7.20 (d, 2 H, Ph), 2.62 (t, 2 H, (CH_2)Ph), 1.58 (m, 2 H, (CH_2)CH_2Ph), 1.26 (m, 18 H, CH_2), 0.88 (t, 3 H, CH_3); IR (CH_2Cl_2) ν(NC) (cm^{-1}) 2130 s.

p-$C_{14}H_{29}C_6H_4NC$. Yield = 40%; ^1H NMR (CD_2Cl_2) 7.29 (d, 2 H, Ph), 7.20 (d, 2 H, Ph), 2.61 (t, 2 H, (CH_2)Ph), 1.58 (m, 2 H, (CH_2)CH_2Ph), 1.26 (m, 22 H, CH_2), 0.88 (t, 3 H, CH_3); IR (CH_2Cl_2) ν(NC) (cm^{-1}) 2127 s.

Synthesis and Characterization of Metal Complexes [Pt(p-$CNC_6H_4C_nH_{1n+1}$)$_4$][Pt(CN)$_4$]. Double-complex salts were prepared by the method reported by Nagel.[11] Syntheses were performed under either argon or N_2 atmospheres, using standard Schlenk techniques. Acetonitrile was distilled from P_2O_5 under N_2. [(n-Bu)$_4$N]$_2$[Pt(CN)$_4$] was prepared from $K_2[Pt(CN)_4]\cdot 3H_2O$ (Aldrich) and [(n-Bu)$_4$N]Br (Aldrich) using literature methods.[12] All other reagents were used as received.

The synthesis of [Pt(p-$CNC_6H_4CH_3$)$_4$][Pt(CN)$_4$] is given as an example. A solution containing 0.270 g (2.30 mmol) of p-tolylisocyanide and 0.152 g (0.436 mmol) of *cis*-$(CH_3CN)_2PtCl_2$ in 20 mL of CH_3CN was stirred under argon for 20 min. To this, 0.753 g (0.960 mmol) of solid [(n-Bu)$_4$N]$_2$[Pt(CN)$_4$] was added with vigorous stirring, resulting in the immediate formation of a blue precipitate. After stirring the solution for 1 h, the solid was collected on a medium frit and washed with three 10 mL portions of cold acetonitrile. The blue solid was dried overnight in vacuo to yield 0.339 g of product.

[Pt(p-$CNC_6H_4CH_3$)$_4$][Pt(CN)$_4$]. Yield = 81%; mp 185−189 °C (dec); IR (film, cm^{-1}) ν(R−NC) = 2258s, 2215w, ν(CN) = 2126m; vis−NIR (film) λ_{max} = 744 nm. Anal. Calcd for $C_{36}H_{28}N_8Pt_2$: C, 44.91; H, 2.93; N, 11.64. Found: C, 44.20; H, 2.72; N, 11.40.

[Pt(p-$CNC_6H_4C_6H_{13}$)$_4$][Pt(CN)$_4$]. Yield = 65%; mp 155−158 °C (dec); IR (film, cm^{-1}): ν(R−NC) = 2258s, 2217w, ν(CN) = 2126m; vis−NIR (film) λ_{max} = 841 nm. Anal. Calcd for $C_{56}H_{68}N_8Pt_2$: C, 54.10, H, 5.51; N, 9.01. Found: C, 54.07; H, 5.31; N, 9.03.

[Pt(p-$CNC_6H_4C_{10}H_{21}$)$_4$][Pt(CN)$_4$]. Yield: 84%; mp 143−147 °C (dec); IR (film, cm^{-1}) ν(R−NC) = 2256s, 2219w, ν(CN) = 2126m; vis−NIR (filter paper) λ_{max} = 746 nm. Anal. Calcd for $C_{72}H_{100}N_8Pt_2$: C, 58.92; H, 6.87; N, 7.63. Found: C, 59.16; H, 6.74; N, 7.33.

[Pt(p-$CNC_6H_4C_{12}H_{25}$)$_4$][Pt(CN)$_4$]. Yield = 53%; mp 130−134 °C (dec); IR (film, cm^{-1}) ν(R−NC) = 2255s, 2217w, ν(CN) = 2125m; vis−NIR (filter paper) λ_{max} = 764 nm. Anal. Calcd for $C_{80}H_{116}N_8Pt_2$: C, 60.81; H, 7.40; N, 7.09. Found: C, 60.99; H, 7.39; N, 7.04.

[Pt(p-$CNC_6H_4C_{14}H_{29}$)$_4$][Pt(CN)$_4$]. Yield = 20%; mp 108−110 °C (dec); IR (film, cm^{-1}) ν(R−NC) = 2256s, 2212w, ν(CN) = 2125m; vis−NIR (filter paper) λ_{max} = 690 nm. Anal. Calcd for $C_{88}H_{132}N_8Pt_2$: C, 62.46; H, 7.86; N, 6.62. Found: C, 63.94; H, 8.23; N, 6.14.

Instrumental Techniques. Vis−NIR absorption spectra were recorded with a Tracor Northern TN-6500 rapid scan diode-array spectrometer with a tungsten lamp light source[13] or with a Nicolet Magna 550 NIR spectrometer. Emission spectra in the NIR region (700−1300 nm) were recorded with a SPEX 112X spectrofluorometer equipped with an InGaAs photodiode operated in intensity mode. The signal was modulated using a Stanford Research Systems SR510 lock-in amplifier and SR540 optical chopper. An Oriel 57385 short-bandpass filter was positioned in the excitation beam to decrease noise. Spectra were corrected for monochromator and detector response after a background spectrum had been subtracted. Sample films of the double-complex salts were coated on 3.0 × 0.5 cm filter paper strips from hexane suspensions as previously described. Care was taken to ensure that initial spectra were of films in the "dry" condition; usually this condition was obtained by pumping on a prepared sample strip overnight under high vacuum. A coated strip was held against the inside wall of a four-sided quartz cell by a copper spring. A beaker was placed inside the cell to contain the solvents. After solvent was added to the beaker, the cell was covered, and at least 5 min was allowed for the equilibrium vapor pressure to be established before spectra were taken. Although the broadness of both the absorption and emission bands observed for these compounds causes a relatively large (±5 nm) uncertainty in the peak maxima, the reproducibility of the line shapes is much higher than this value.

Infrared absorption spectra were obtained by an attenuated total reflectance (ATR) method using a Nicolet Magna-IR System 550 spectrometer, equipped with a ZnSe trough HATR cell from PIKE Technologies. Data were processed using OMNIC 1.2 software. Sample films were coated on the ZnSe crystal from either a $CHCl_3$ solution or hexane suspension. Films of the double-complex salts were washed with acetone prior to taking spectra to remove impurities and decomposition products. A beaker was placed on the ZnSe crystal mount to contain the solvents. After solvent was added to the beaker, the film and crystal mount were covered, and numerous spectra were recorded before and after the equilibrium vapor pressure was established.

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(11) (a) Nagel, C. C. U.S. Patent 4,834,909. (b) Nagel, C. C. U.S. Patent 4,826,774. Related compounds have also been synthesized: (c) Isci, H.; Mason, W. R. *Inorg. Chem.* **1974**, *13*, 1175−1180. (d) Keller, H. J.; Lorenz, R. *J. Organomet. Chem.* **1975**, *102*, 119−122. (e) Keller, H. J.; Lorenz, R. *Z. Naturforsch. B* **1976**, *31B*, 565−568.

(12) Mason, W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5721.

(13) Bullock, J. P.; Mann, K. R. *Inorg. Chem.* **1989**, *28*, 4006.

Results and Discussion

The double-complex salts were prepared by the modification of a previously described method.[5,11] Addition of the appropriate isocyanide to a solution of *cis*-$(CH_3CN)_2PtCl_2$ in acetonitrile was followed by addition of $[(n\text{-}Bu)_4N]_2[Pt(CN)_4]$. The complexes were isolated as blue, mostly insoluble solids in yields that ranged from 20 to 85%. The compounds are stable for at least months in the solid state, but as reported by Keller and Lorenz[11e] for similar compounds, we observed a slow decomposition reaction for solutions of the $[Pt(arylisocyanide)_4][Pt(CN)_4]$ complexes in chlorinated solvents. This reaction produces *cis*-$Pt(arylisocyanide)_2(CN)_2$. The decomposition rate decreases in the order $CH_2Cl_2 > CHCl_3 \gg CCl_4$. This decomposition reaction is much slower ($t_{1/2}$ is on the order of 8 days for CH_2Cl_2) than the corresponding reaction observed for the $[Pt(arylisocyanide)_4][Pd(CN)_4]$ analogues ($t_{1/2}$'s on the order of hours).

All of the compounds studied in the solid state exhibit a prominent electronic transition at the edge of the visible, extending well into the near-infrared spectral region (Table 1). We assign the absorption to a spin allowed component of the $d\sigma^* \rightarrow p\sigma$ transition that arises from a linear stack of alternating cations and anions.[6,7] Vis–NIR absorption spectra of the homometallic double-complex salts ($[Pt(arylisocyanide)_4][Pt(CN)_4]$) of solid-state dispersions on filter paper show that the position of the low-energy band varies somewhat unpredictably with the alkyl substituent chain length. We believe that this variation is due to changes in the stacking interactions between the cations and anions caused by crystal packing effects rather than differences in the electronic effect of the substituent on the cation energy levels. In comparison to the PtPd analogue compounds, the low-energy band is shifted approximately 5000 cm^{-1} lower in energy. This large shift is indicative of an increase in the M–M interaction between the cation and anion in the homometallic compounds.[14] Additionally, the compounds exhibit an intense emission band in the NIR (Table 1). These emission bands are (tentatively) assigned to a spin-allowed component of the $p\sigma \rightarrow d\sigma^*$ transition; a more definitive assignment must await emission lifetime measurements. In any event, these compounds join a very select group of transition-metal complexes that emit in the NIR spectral region.[15]

Table 1. Absorption and Emission λ_{max} for Solid-State Films of $[Pt(arylisocyanide)_4][Pt(CN)_4]$ (arylisocyanide = $p\text{-}CNC_6H_4C_nH_{2n+1}$; n = 1, 6, 10, 12, 14)

n	abs max (nm)	emission max (nm)
1	744	958
6	841	910
10	746	972
12	764	912
14	690	876

Table 2. Absorption and Emission λ_{max} and Vapochromic Shifts for Solid-State Films of $[Pt(p\text{-}C_{10}H_{21}PhNC)_4][Pt(CN)_4]$

solvent	abs max (nm)	vapochromic shift (nm)[a]	emission max (nm)	vapochromic shift (nm)[a]
none	746		944	
water	746	0	b	b
MeOH	757	11	946	2
EtOH	787	41	992	48
2-PrOH	782	36	974	30
Et_2O	787	41	970	26
CH_3CN	809	63	980	36
hexanes	775	29	950	6
acetone	800	54	986	42
benzene	801	55	990	46
CH_2Cl_2	811	65	976	32
$CHCl_3$	837	91	1018	74

[a] Vapochromic shift = λ_{max} (VOC) − λ_{max} (none). [b] Not measured.

The stacked nature of the $[Pt(arylisocyanide)_4][Pt(CN)_4]$ solids is further supported by the dramatic temperature dependence of the NIR absorption band. For example, upon cooling a "dry" film of $[(p\text{-}C_{10}H_{21}C_6H_4NC)_4Pt][Pt(CN)_4]$ from room temperature to 77 K, the absorption band maximum shifts from 746 to 846 nm, and the emission band maximum shifts from 944 to 1094 nm. This diagnostic red-shift is observed in the solid-state spectra of stacked complexes because the thermal lattice contraction caused by cooling results in shorter metal–metal distance.[6,16]

Qualitatively, one expects the response of $[Pt(arylisocyanide)_4][Pt(CN)_4]$ to VOCs as a function of chain length to be similar to the $[Pt(arylisocyanide)_4][Pd(CN)_4]$ compounds previously studied. For example, for the response of $[Pt(arylisocyanide)_4][Pd(CN)_4]$ to 1-propanol the ordering was $10 \gg 6 > 1 \sim 12 > 14$. Typical solvents of low polarity are detected more readily by compounds with a larger n value, while the detection of solvents more polar than 1-propanol is better with a smaller n value. The time scale of VOC sorption is also similar for the two sets of compounds ($t_{1/2} <$ 500 ms, in absorption experiments). In general, the NIR shifts exhibited by $[Pt(p\text{-}C_{10}H_{21}C_6H_4NC)_4][Pt(CN)_4]$ are 2–3 times greater than those observed for the $Pd(CN)_4^{2-}$ salt[5] (see Table 2). Among the solvents we have tested, ethanol, 2-propanol, acetonitrile, and acetone affect the peak position of the $Pt(CN)_4^{2-}$ salt substantially more than they do the $Pd(CN)_4^{2-}$ salt, but the general order of solvent effects is the same for both $M(CN)_4^{2-}$ salts. The increase in the shift observed for the $Pt(CN)_4^{2-}$ salts suggests that the solvent interacts with the chromophore relatively more strongly in the $Pt(CN)_4^{2-}$ salt than in the $Pd(CN)_4^{2-}$ salt.

As in the case of the $[Pt(arylisocyanide)_4][Pd(CN)_4]$ compounds, we have studied in greatest detail the vapochromic shifts in the low-energy NIR absorption and emission bands of solid-state films of $[Pt(p\text{-}C_{10}H_{21}C_6H_4NC)_4][Pt(CN)_4]$ (the n = 10 compound). This

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(14) It is commonly observed that the energy of the lowest $d\sigma^* \rightarrow p\sigma$ transition decreases for elements of the third transition series; see: (a) Smith, T. P. Ph.D. Dissertation, California Institute of Technology, 1982.

(15) Many minerals and simple ionic solids that contain transiton-metal ions emit in the NIR spectral region; the following references are for transition-metal complexes: (a) Yao, Q.; Maverick, A. W. *Inorg. Chem.* **1988**, *27*, 1669. (b) Reber, C.; Güdel, H. U. *J. Lumin.* **1988**, *42*, 1. (c) Mosseri, S.; Mialocq, J. C.; Perly, B.; Hambright, P. *J. Phys. Chem.* **1991**, *95*, 2196. (d) Bilsel, O.; Rodriguez, J.; Milam, S. N.; Gorlin, P. A.; Girolami, G. S.; Suslick, K. S.; Holten, D. *J. Am. Chem. Soc.* **1992**, *114*, 6528. (e) Stranger, R.; Moran, G.; Krausz, E.; Dubicki, L.; Güdel, H.; Furer, N. *Inorg. Chem.* **1992**, *31*, 2860. (f) Vincze, L.; Friesen, D. A.; Mezyk, S. P.; Waltz, W. L. *Inorg. Chem.* **1992**, *31*, 4950. (g) Herren, M.; Güdel, H. U. *Inorg. Chem.* **1992**, *31*, 3683. (h) Matsui, K.; Nazeeruddin, M. K.; Humphrybaker, R.; Gratzel, M.; Kalyanasundaram, K. *J. Phys. Chem.* **1992**, *96*, 10587. (i) Richter, M. M.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 5762. (j) Davis, M.; Reber, C. *J. Lumin.* **1994**, *60*, 1. (k) Juris, A.; Balzani, V.; Campagna, S.; Denti, G.; Serroni, S.; Frei, G.; Güdel, H. U. *Inorg. Chem.* **1994**, *33*, 1491. (l) Savoie, C.; Reber, C.; Belanger, S.; Beauchamp, A. L. *Inorg. Chem.* **1995**, *34*, 3851.

(16) Palmans, R.; Frank, A. J.; Houlding, V. H.; Miskowski, V. M. *J. Mol. Catal.* **1993**, *80*, 327.

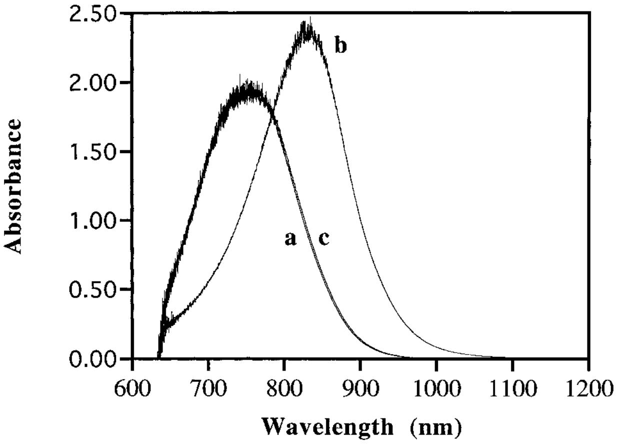

Figure 2. Vapochromic response of a thin film of [Pt-($CNC_6H_4C_{10}H_{21}$)$_4$][Pt(CN)$_4$] on a ZnSe ATR crystal. (a) "Dry" film; (b) film in the presence of dichloromethane vapor; (c) removal of dichloromethane shifts the spectrum back to the "dry" state. Curves (a) and (c) are virtually superimposable. The spectra are corrected for "ATR penetration depth effects".[19]

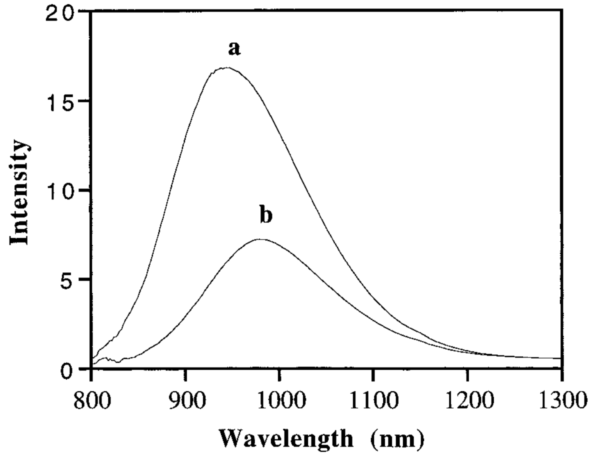

Figure 3. Room-temperature emission spectra of [Pt-($CNC_6H_4C_{10}H_{21}$)$_4$][Pt(CN)$_4$] dispersion on filter paper excited at λ_{ex} = 725 nm. (a) "dry" sample; (b) same sample in the presence of air saturated with CH_2Cl_2 vapor.

compound is responsive and shows high sensitivity and stability in its vapochromic response to a wide range of VOC compounds. As summarized in Table 2, the absorption bands of the solid-state films of [Pt(p-$C_{10}H_{21}C_6H_4NC$)$_4$][Pt(CN)$_4$] shift from 11 to 91 nm (190–1500 cm^{-1}) lower in energy upon exposure to VOCs. The particularly large change in the vis-NIR absorption spectrum that occurs when dichloromethane contacts a film of [Pt(p-$C_{10}H_{21}C_6H_4NC$)$_4$][Pt(CN)$_4$] on an ATR crystal is shown in Figure 2. The peak shifts nearly isosbestically from 746 nm to 811 nm as the VOC equilibrates with the solid. Repeated cycles of dichloromethane exposure and removal lead to no apparent changes in the spectral sequences observed. A similar shift occurs in the emission bands of the solid-state films of [Pt(p-$C_{10}H_{21}C_6H_4NC$)$_4$][Pt(CN)$_4$] (Figure 3, Table 2), but the shifts in the emission band are somewhat smaller than those observed for the absorption band and range between 2 and 72 nm (22–770 cm^{-1}) lower in energy upon exposure to VOCs.

IR spectroscopy studies were useful for characterizing interactions between the cations and anions in the solid compounds. The solid-state infrared spectrum of a dry [Pt(p-$CNC_6H_4C_{10}H_{21}$)$_4$][Pt(CN)$_4$] film shows single bands at 2259 (ν(CNR)) and 2125 cm^{-1} (ν(CN)). The ν(CN) isocyanide stretching frequency in the [Pt($CNC_6H_4C_{10}H_{21}$)$_4$][Pt(CN)$_4$] compound is substantially shifted from the free ligand value (2130 cm^{-1}). This shift to higher energy is consistent with strong σ donation of the $CNC_6H_4C_{10}H_{21}$ isocyanide ligand to the Pt(II) and is in agreement with ν(CN) isocyanide stretching frequencies previously reported for other [Pt(CNR)$_4$]$^{2+}$ complexes with noninteracting counterions.[11c,17] The modest shift in the ν(CN) cyanide stretching frequency for [Pt-($CNC_6H_4C_{10}H_{21}$)$_4$][Pt(CN)$_4$] (2125 cm^{-1}) relative to ν-(CN) observed (2118 cm^{-1}) for the [(C_4H_9)$_4$N]$_2$[Pt(CN)$_4$] precursor suggests that there is little ground-state charge transfer between anion and cation imposed by the Pt–Pt stacking of the double-complex salt structure.

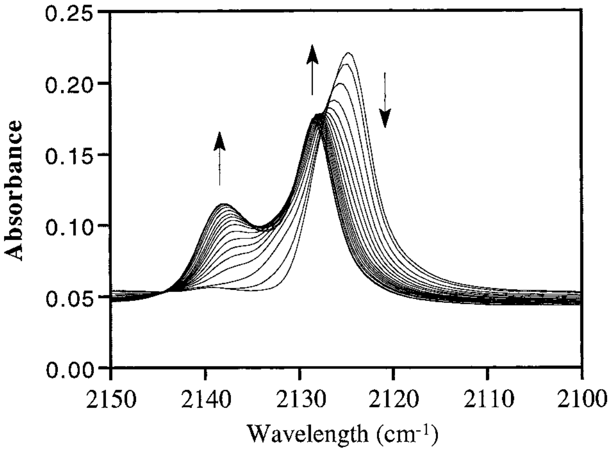

Figure 4. ATR-FTIR spectral study of [Pt($CNC_6H_4C_{10}H_{21}$)$_4$]-[Pt(CN)$_4$] as the air inside the sample compartment is saturated with CH_3OH vapor. Arrows indicate the direction of change. The first 12 spectra were taken at ca. 16 s intervals; the last 5 spectra were at 120 s intervals. Spectra are uncorrected for "ATR penetration depth effects".

IR spectroscopy was also useful for gaining insight into the nature of the interactions between the VOC and the components of the solid that lead to the vapochromic shifts.[5,18] These interactions could be due to a complicated mix of lypophilic, dipole–dipole, and/or hydrogen-bonding interactions. Exposure of a [Pt($CNC_6H_4C_{10}H_{21}$)$_4$]-[Pt(CN)$_4$] film to any of the VOC vapors in Table 2 results in no appreciable shift in the ν(CN) isocyanide stretching frequency, but the ν(CN) cyanide stretch exhibits a reversible shift to higher frequency of 0–15 cm^{-1} (see Table 3). The magnitude of these shifts is on the order of the 7 cm^{-1} shift that occurs when the solid-state structure is formed from the ionic precursors. As in the case of the vis–NIR absorption band, removal of the VOC vapor source causes the IR spectrum to revert to that of the dry film for all the VOCs studied. The largest shifts in the ν(CN) cyanide stretch are produced by VOCs capable of hydrogen bonding, while aprotic VOCs cause little or no ν(CN) shifts. In addition to the shift, exposure of [Pt($CNC_6H_4C_{10}H_{21}$)$_4$][Pt(CN)$_4$] to $CHCl_3$ or alcohol vapor (Figure 4) causes the ν(CN) cyanide band to split into two bands spaced 5–10 cm^{-1} apart. The two ν(CN) bands in the VOC-saturated [Pt-($CNC_6H_4C_{10}H_{21}$)$_4$][Pt(CN)$_4$] IR spectrum indicate that

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Table 3. Cyanide CN Stretching Frequencies and Vapochromic Shifts[a] upon Exposure to VOCs for $[Pt(CNC_6H_4C_{10}H_{21})_4][Pt(CN)_4]$

VOC	ν(CN), cm^{-1}	vapochromic shift, cm^{-1}
none	2125	
water	2125	0
hexanes	2125	0
carbon tetrachloride	2126	1
diethyl ether	2126	1
benzene	2126	1
acetone	2126	1
dichloromethane	2127	2
acetonitrile	2127	2
chloroform	2127, 2132	2, 7
2-Propanol	2128, 2135	3, 10
ethanol	2128, 2136	3, 11
methanol	2128, 2138	3, 13
1,1,1-trifluoroethanol	2130, 2140	5, 15

[a] Vapochromic shift = $\nu(CN)_{VOC} - \nu(CN)_{none}$.

at least two different cyanide environments per $[Pt(CN)_4]^{2-}$ unit are present in the solid. The combined integrated area under these bands is nearly equal to that for the single ν(CN) band of the dry film, indicating that the double-complex salt remains in the solid phase upon sorption of the VOC.[19] This observation is also consistent with our previously reported X-ray powder diffraction studies of $[Pt(CNC_6H_4C_{10}H_{21})_4][Pd(CN)_4]$, which showed that the crystallinity of the double-complex salt is not significantly affected by the sorption of VOCs.[5]

The shifts that we report for the cyanide ν(CN) stretch are analogous (but somewhat smaller) than the irreversible shifts reported for solid $K_2Ni(CN)_4$[20] and $Fe(phen)_2(CN)_2$ (phen = 1,10-phenanthroline)[21] when they are exposed to the powerful Lewis acid BF_3. As in the case of the BF_3 results, we suggest that the ν(CN) *shift* results from interactions involving the cyanide lone pair on N and the VOC guest molecule. Although this simple interaction model suggests that a direct correlation between the ν(CN) shift and VOC Lewis acidity (or hydrogen-bond-donating ability) should be observed, two particularly intriguing results with benzene and water suggest that the vapochromic shifts in the IR and the vis–NIR may not correlate perfectly and may arise from more complicated interactions within the solid or at the solid/gas interface. For the $n = 10$ compound, benzene exhibits a relatively large vapochromic shift in the NIR but a small ν(CN) cyanide shift, while water elicits no vapochromic response. The benzene results suggest that lypophilic interactions with the isocyanide ligands that do not result in substantial ν(CN) shifts may nevertheless be important in producing vapochromic shifts. Solid-state ^{13}C NMR studies are planned to address this issue. In the case of the results with the strong H-bonder water, the lack of a vis–NIR vapochromic response or a ν(CN) shift strongly suggests that water is unable to penetrate the solid. The network produced by stacking the long *n*-decyl chains of the isocyanide ligands in the structure may produce a hydrophobic barrier at the solid/gas interface through which water is unable to pass. Further studies will be needed to address this (presumably) kinetic effect.

Conclusions

We have synthesized the homometallic $[Pt(arylisocyanide)_4][Pt(CN)_4]$ analogues for comparison with the previously communicated mixed metal $[Pt(arylisocyanide)_4][Pd(CN)_4]$ compounds. Vis–NIR and IR studies allow several conclusions to be drawn:

$[Pt(arylisocyanide)_4][Pt(CN)_4]$ compounds exhibit strong absorptions and emission bands in the NIR spectral region due to excitations of an electronic transition that is characteristic of M–M chains of d^8 metal ions. The NIR emission properties are particularly noteworthy.

Solutions of the Pt–Pt compounds in chlorinated solvents are more stable than those of the PtPd analogues.

The absorption and emission bands of the PtPt compounds are substantially red-shifted from those observed for the PtPd compounds.

The position of $\lambda_{max\ abs}$ in the dry films and the magnitude of the vapochromic effect in the vis–NIR are an undetermined function of the alkyl substituent chain length.

IR spectra of solid films suggest that VOCs capable of hydrogen bonding interact strongly with the $Pt(CN)_4^{2-}$ group in the solid.

Exposure to nonpolar VOCs (i.e., benzene) does not cause large shifts in the ν(CN) IR spectral region but nevertheless results in substantial vapochromic effects in the NIR. The vapochromism in this case must be attributed to lypophilic interactions.

The compounds are unresponsive to water vapor in the NIR and in the IR spectral regions. This may be due to important hydrophobic interactions at the solid/gas interface.

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